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MODELING THE TRANSPORT AND FATE OF MERCURY IN AN URBAN LAKE (ONONDAGA LAKE, NY)

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Abstract. A mass balance model was developed to simulate mercury (Hg) cycling in Onondaga Lake, New York. MERC4, a U.S. Environmental Protection Agency model of the physical and biogeochemical transport and transformation of Hg, was modified by the addition of input from two supporting models (Fish Bioenergetics Model 2 and a lake eutrophication model) to model the transport of Hg into and out of plankton and fish. The model calculates the concentrations of total Hg, methylmercury, elemental Hg, and ionic Hg in both dissolved and particulate forms in the water column. The model was calibrated to an extensive data set of temporally and spatially variable Hg concentrations in Onondaga Lake in 1992. In addition to standard transport processes of advection and dispersion included in MERC4, the Onondaga Lake Mercury Model includes remineralization to simulate release of Hg from settling particulates before incorporation into sediment. The model provides an analytical framework for understanding and predicting the behavior of Hg in Onondaga Lake and has potential use in evaluating the relative impact of different source control and remedial alternatives.

1. Introduction

As the understanding of mercury (Hg) cycling in the environment has evolved, several attempts have been made to model these dynamic processes. For example, Harris (1991) developed a model that follows Hg cycling in aquatic systems and the Electric Power Research Institute developed the Mercury Cycling Model (Tetra Tech, 1992; Hudson *et al.*, 1992) to examine Hg cycling in Wisconsin seepage lakes. Both models are dynamic, mechanistic, mass balance models. Recently, the kinetic subroutine pertinent to Hg from the Mercury Cycling Model was incorporated into WASP4 (Water Quality Analysis Simulation Program; U.S. EPA, 1991). The resulting model, MERC4 (ASCI, 1992), can simulate Hg cycling (but not bioaccumulation) in a variety of aquatic systems (e.g., rivers, lakes, estuaries).

The Onondaga Lake Mercury Model (OLMM) was developed as part of a large remedial investigation and feasibility study of Onondaga Lake, New York, a slightly alkaline, hypereutrophic lake which received historical discharges of Hg from two Hg-cell chloralkali plants. One purpose of the OLMM was to provide an analytical framework for understanding and predicting the behavior of Hg in Onondaga Lake. MERC4, the principal model in the OLMM, was modified to be supported by the Fish Bioenergetics Model 2 (FBM2) (Hewett and Johnson, 1991) to track Hg in fishes, and a lake eutrophication model (HydroQual, 1994) to estimate phytoplankton populations and settling rates.

This paper describes construction of the OLMM and results of its calibration to an extensive data set from the 1992 Onondaga Lake field investigation (Henry *et al.*, 1995; Jacobs *et al.*, 1995). Bioaccumulation is only briefly described because final calibration is incomplete. Bioaccumulation in the OLMM will be described in more detail in a later publication.

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2. General Components of the Onondaga Lake Mercury Model

2.1. MERC4

MERC4 is implemented as a kinetic subroutine for Hg transformations that is linked with the transport modeling routines of the WASP4 model (U.S. EPA, 1991). The kinetics add the ability to represent sorption of Hg to solids and complexation of Hg with dissolved organic carbon, transformations among Hg species (e.g., reduction, methylation), and complexation of Hg with other water quality constituents (e.g., hydroxide, chloride, sulfide). For the purpose of modeling Onondaga Lake, the transport modeling capabilities of MERC4 were extended to include remineralization of Hg species (i.e., release of Hg from particles in the water column), and the MERC4 kinetic routines were extended to include accumulation and release of Hg by plankton and fish. Figure 1 illustrates the conceptual framework for the OLM.

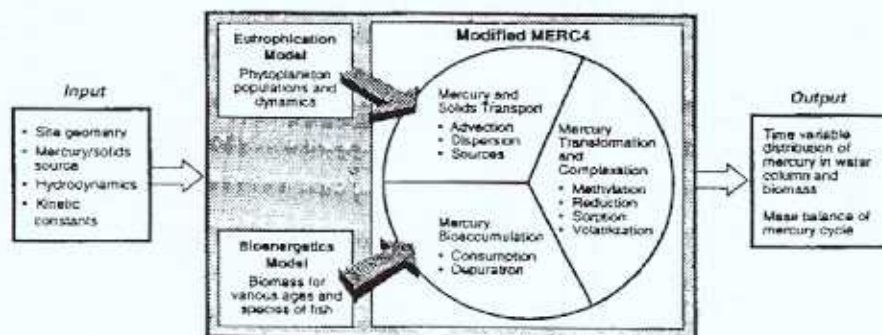


Fig. 1. Conceptualization of the Onondaga Lake Mercury Model

2.2. FBM2

FBM2 is a set of mathematical equations that describe individual fish consumption, respiration, specific dynamic action, egestion, excretion, and reproduction, and that balance the energy requirements of these processes to determine individual growth. These processes, on a population basis, are used in the modified kinetics of MERC4 to model accumulation and depuration of Hg in fish.

2.3. EUTROPHICATION MODEL

The eutrophication model of Onondaga Lake is implemented as a kinetic expression that utilizes environmental conditions (i.e., nutrients, sunlight, and temperature) to simulate the dynamics of phytoplankton biomass. Biomass dynamics, such as growth, respiration, and settling, are provided to MERC4 as input.

3. Development of the Onondaga Lake Mercury Model

3.1. SEGMENTATION

Onondaga Lake was conceptually divided into 3 segments to represent different water column regimes. These regimes are 1) the littoral zone (i.e., the nearshore epilimnion in contact with lake-bottom sediments), 2) the pelagic zone (i.e., the epilimnion underlain by the hypolimnion), and 3) the profundal zone (i.e., the hypolimnion underlain by profundal sediments). Environmental conditions and Hg transformation rates may differ in each of these segments.

3.2. TRANSPORT

3.2.1. Advection

A water balance for Onondaga Lake was computed using the weekly averages of measured tributary inflows (Henry *et al.*, 1995), estimated evaporation, measured precipitation in Syracuse (NOAA, 1992), estimated groundwater inflow, and estimated changes in the lake volume based on the surface area of the lake and the elevation of the lake recorded by the U.S. Geological Survey (USGS, 1993). Groundwater contributed 0.3 percent of total water inflow and was omitted from the water balance. The excess water was assigned as outflow to the Seneca River. All outflows were calculated to be positive.

Surface water inflows, with the exception of Ninemile Creek, enter the littoral segment and mix with the pelagic segment. Because of its high chloride content and resulting elevated density (HydroQual, 1994), flow from Ninemile Creek is specified to enter the lake by way of the profundal segment to simulate plunging. The lake outflow leaves through the littoral segment.

3.2.2. Dispersion

Dispersive mixing between the profundal and pelagic segments in the OLMM is used to simulate spring and fall turnover and summer stratification. Increased mixing coefficients are specified during turnover to nearly homogenize the epilimnion and hypolimnion. Decreased mixing is specified during stratification to reduce mixing across the thermocline. As a result, the concentration of Hg increases in the profundal segment simulating the concentration increase in the hypolimnion observed in the 1992 data (Jacobs *et al.*, 1995).

3.2.3. Settling

The settling and deposition of three types of particles are specified in the OLMM. These particles represent inorganic (fluvial) solids, phytoplankton, and detritus. No estimates of resuspension were available; therefore, a net settling term was used based on data from sediment traps deployed in both the pelagic and profundal zones of the lake (Henry *et al.*, 1995). Settling rates of inorganic particles were estimated from mass accumulation rates in sediment traps and total suspended solids concentrations in the overlying water. The estimated settling rates of phytoplankton and detritus were provided by the eutrophication model of Onondaga Lake (HydroQual, 1994). Final settling rates were adjusted during calibration.

3.2.4. Remineralization

Remineralization is defined in the OLMM as the release of Hg from settling particles in profundal water close to the sediment-water interface. Hurley *et al.* (1994) have described this process for Little Rock Lake, Wisconsin. Remineralization of Hg in Onondaga Lake is supported by the

comparison of gross and net Hg sedimentation as discussed in Henry *et al.* (1995). Resuspension of bottom sediments can also result in greater gross than sedimentation; however, resuspension was considered insignificant in the profundal waters of Onondaga Lake where the water column is quiescent in this region. A temporally variable recycling fraction is applied to each type of particle. Recycling fractions were adjusted during calibration.

3.3. LOADS

Tributaries, sediments, groundwater, and atmospheric deposition all contribute Hg to Onondaga Lake. The contribution of each was calculated from field data, experimental data, and literature (Henry *et al.*, 1995). All Hg loads, except dissolved flux from sediment, were specified as fixed inputs. Although Hg release from the sediment is likely to be dependent upon factors that affect the rate of Hg methylation (e.g., dissolved oxygen concentration), there are insufficient data from Onondaga Lake to characterize this functional relationship. As a result, fluxes of Hg from sediment were adjusted during calibration.

3.4. MERCURY KINETICS

MERC4 recognizes four types of Hg (i.e., elemental, methyl-, ionic, and inert) to model Hg cycling. However, the distinction between ionic (i.e., reactive) and inert (i.e., non-reactive) Hg is highly dependent on the analytical technique used to make the measurement (Bloom, 1994). In addition, the implications of this distinction on Hg transformation processes in the environment are unknown. Therefore, the "reactive" and "non-reactive" fractions (both available from the Onondaga Lake data set) were combined into a single Hg type (hereafter referred to as ionic Hg) for the modeling effort. In this paper, ionic Hg refers to all Hg species, with the exception of elemental Hg, CH₃Hg, and dimethylmercury [(CH₃)₂Hg] which can be measured directly. The values for ionic Hg were derived as follows:

$$Hg_{\text{ionic}} = Hg_{\text{total}} - [\text{elemental Hg} + CH_3Hg + (CH_3)_2Hg]$$

The Hg cycle used in the application of MERC4 to Onondaga Lake is presented in Figure 2. Three Hg species (i.e., elemental, methyl-, and ionic) are modeled. The model includes two transformations between species (net methylation and reduction), sorption to three particle types (fluvial, phytoplankton, and detritus), and volatilization. Because there are no site-specific data on the concentrations or equilibrium constants for Hg complexes (e.g., with chloride, sulfide, hydroxide) and little information on the participation of these complexes in transformation reactions or sorption equilibria, each Hg species is considered as a pool of various complexes. All members of a pool are presumed to participate equally in any transformation or sorption/desorption processes.

3.4.1. Transformation

Two transformations between Hg species are explicitly modeled. The concomitant processes of Hg methylation and methylmercury (CH₃Hg) demethylation were combined as net Hg methylation. While the two processes can be differentiated analytically (Furutani and Rudd, 1980; Ramlal *et al.*, 1986), the current method of choice for measuring methylation rates (Gilmour, 1995), which was used in Onondaga Lake (Henry *et al.*, 1995), yields an estimate of net CH₃Hg production. Based on the literature (Winfrey and Rudd, 1990; Gilmour and Henry, 1991) and experimental data (Henry

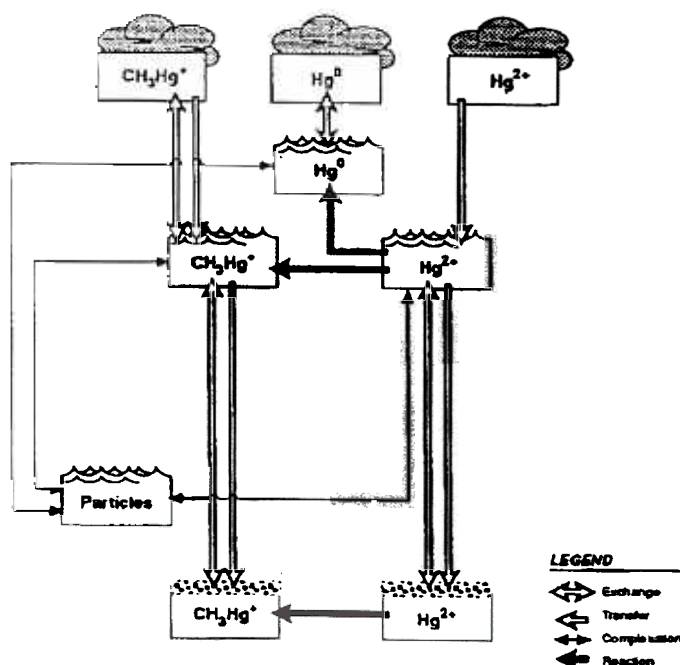


Fig. 2. Simplified mercury cycling in the Onondaga Lake Mercury Model

et al., 1995), net methylation is modeled as increasing with temperature and occurring at low dissolved oxygen concentrations (in the hypolimnion). The rate of methylation of ionic Hg was adjusted during calibration until model calculations of methylation on a volumetric basis compared well with experimental observations made in Onondaga Lake during 1992 (Henry *et al.*, 1995).

Reduction of ionic Hg to elemental Hg is modeled as increasing with temperature and occurring under oxic conditions (in the epilimnion). The rate of reduction was adjusted during calibration so that calculated concentrations of elemental Hg most effectively simulated observed elemental Hg concentrations.

Other environmental characteristics in Onondaga Lake that may influence methylation and reduction rates in the water column (e.g., pH, organic carbon, ionic Hg speciation) were not included in the water-column methylation reaction. Insufficient site-specific or literature data were available to distinguish the form of the functional relationship (if any) between these parameters and the rate of CH_3Hg production in Onondaga Lake.

3.4.2. Sorption

A site-specific partition coefficient for CH_3Hg in phytoplankton was directly computed from field data by dividing the CH_3Hg concentration in phytoplankton by the dissolved CH_3Hg concentration in water. Other site-specific partition coefficients (CH_3Hg -fluvial solids, CH_3Hg -detritus, ionic Hg-fluvial solids, ionic Hg-detritus) were indirectly estimated from field data by dividing the particulate

concentration by the dissolved concentration of the two mercury species (CH_3Hg and ionic Hg). The particulate concentrations were determined as an average over all particulates measured in Onondaga Lake as suspended solids. The final partition coefficients were adjusted during model calibration to optimize the predicted dissolved and total concentrations of total Hg and CH_3Hg in comparison to field observations.

3.4.3. Volatilization

The O'Connor equations for a stagnant lake or pond were selected from options available in MERC4 (ASCI, 1992) to estimate both the liquid and gas film transfer coefficients for volatilization of elemental Hg. This approach calculates a shear velocity based on observed wind speed and liquid and gas film transfer coefficients based on shear velocity, media densities, and Schmidt numbers. The liquid and gas film transfer coefficients are used to estimate the overall transfer rate as a function of the universal gas constant, Henry's law constant, and air temperature.

4. Model Calibration

The OLMM was calibrated to most effectively model water column concentrations of Hg species measured in Onondaga Lake during the April to November field sampling program in 1992 (Jacobs *et al.*, 1995). In general, parameters internal to the lake were manipulated within ranges of observed data. Other inputs and outputs (i.e., loading, atmospheric deposition, groundwater, and volatilization) were specified as described in Henry *et al.* (1995). Tables I and II present the calibrated and observed values for these internal parameters.

TABLE I
Net methylmercury production, dissolved flux, and remineralization rates

| Parameter | Value in the OLMM | | Observed value* |
|--|-------------------|-------------|-----------------|
| | Annual average | Range | |
| Net CH_3Hg production ($\text{ng/L}\cdot\text{day}$) | 0.034 | 0-0.13 | 0.003-0.11 |
| Dissolved flux ($\text{ng/m}^2\cdot\text{day}$) | | | |
| Total Hg | 21 | 8.0-52 | 6.0-50 |
| CH_3Hg | 6.1 | 1.3-25 | -0.3-38 |
| Remineralization ($\text{ng/m}^2\cdot\text{day}$) | | | |
| Total Hg | 2,690 | 1,100-5,480 | -275-500 |
| CH_3Hg | 300 | 25-1,100 | 380-495 |

* Henry *et al.* (1995).

TABLE II
Total mercury and methylmercury flux from Onondaga Lake sediments

| Site | Dissolved oxygen in overlying water ^a (mg/L) | Concentration in 0-4 cm sediment ^b | | Flux ^c (ng/m ² -day) | |
|------|---|---|---------------------------|--|---------------|
| | | Total mercury (mg/kg dry) | Methylmercury (μg/kg dry) | Total mercury | Methylmercury |
| | 2.9 | | | | |
| S73A | 2.6 | 1.08 ± 0.03 | 4.87 ± 0.48 | 5.2 ± 2.1 | |
| S90A | NA ^c | 1.25 ± 0.07 | 3.71 ± 0.18 | 50 ± 22 | |

NA - not analyzed

^a Average during course of experiment.

^b Values are means ± standard error. N=3 unless noted.

^c Samples contained an average of 0.68 μmol sulfide/L.

Final calibrations for total Hg and CH₃Hg in both total (i.e., unfiltered) and dissolved (i.e., filtered) forms are illustrated in Figures 3 and 4, respectively. Data ranges for the hypolimnion reflect the large total Hg and CH₃Hg concentration differences between the thermocline and the lake bottom. With two exceptions, the model simulates the average epilimnetic and hypolimnetic total Hg and CH₃Hg concentrations. First, the calculated hypolimnetic concentrations of total Hg (Figure 3) and ionic Hg (not shown) in early spring do not increase to the levels observed in the 1992 data set. The elevated total Hg and ionic Hg concentrations observed in April may be the result of spring runoff or unexamined mercury cycling processes (e.g., settling of particles) occurring during winter months. Neither calculated nor observed CH₃Hg concentrations are elevated in April, suggesting that little methylation occurs in winter when the water column is aerobic (Walker, 1991).

Second, the model slightly undercalculates the observed epilimnetic concentrations of total Hg (Figure 3) and ionic Hg (not shown) during stratification in late summer. Greater mixing between the epilimnion and hypolimnion at the end of summer would alleviate the discrepancy. However, it would also aggravate the overcalculation of CH₃Hg in the epilimnion during this same period (Figure 4). The reasons for these two exceptions may become clear with further data collection and/or model calibration.

5. Conclusions

The OLM model effectively simulates the concentrations of Hg species and provides a framework for understanding important processes involved in Hg cycling in Onondaga Lake. A real strength of the modeling effort was the ability to calibrate the model to an extensive data set from the 1992 field investigation. In addition, the ability to model the transport and fate of solids and the inclusion of remineralization to simulate release of Hg from settling particles were valuable aspects of the model. The model is general enough to be applicable to other systems, given appropriate data. The OLM model will be used to evaluate the relative impact of different source control and remedial alternatives.

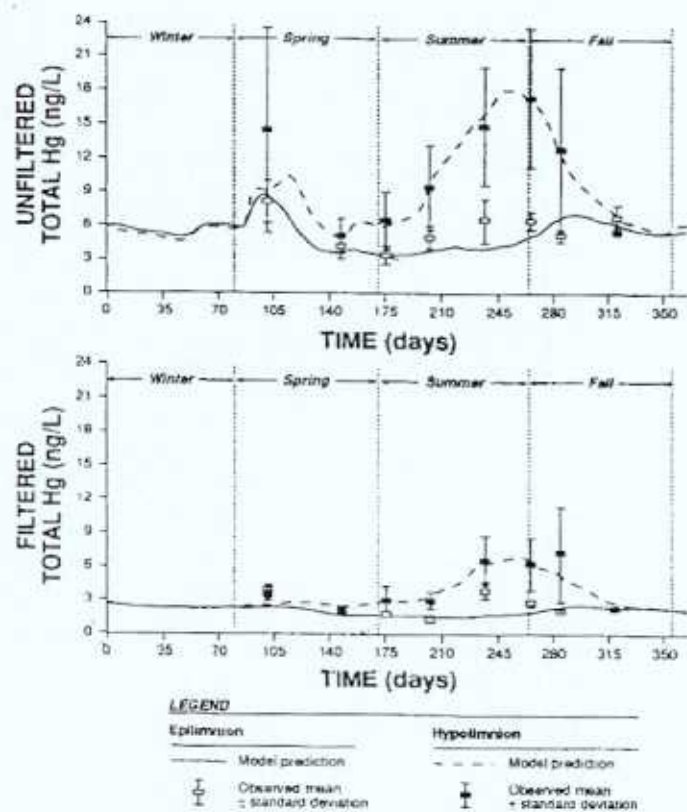


Fig. 3. Observed water column data (Jacobs *et al.*, 1995) and model-calibrated values for total Hg in Onondaga Lake in 1992.

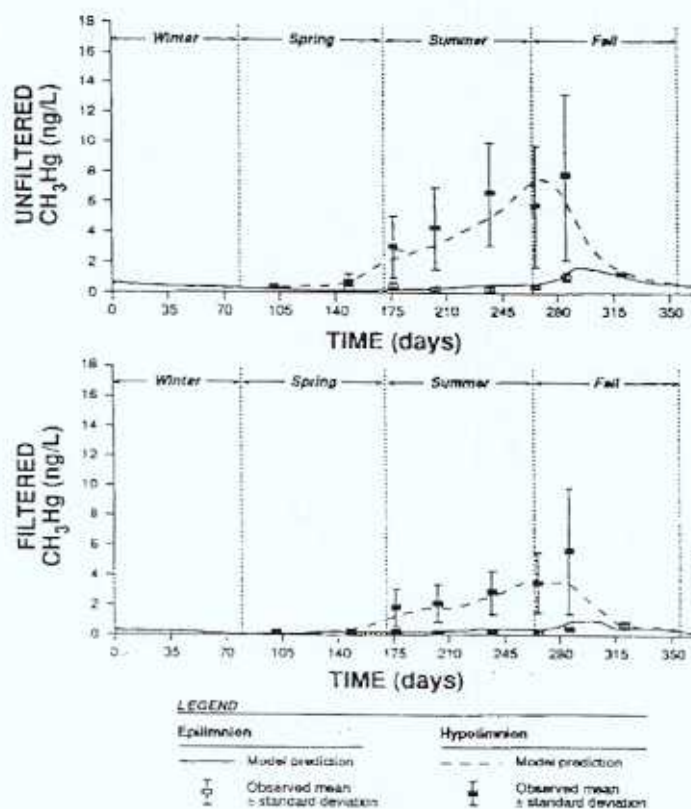


Fig. 4. Observed water column data (Jacobs *et al.*, 1995) and model-calibrated values for CH₃Hg in Onondaga Lake in 1992.

Acknowledgements

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